

Used Fuel Disposition Campaign

Coupled Processes and Reactive Transport in Engineering Barrier Systems

**Jonny Rutqvist, Carl Steefel, Jim Davis, Ian Bourg,
Ruth Tinnacher, Juan Galindez Jens Birkholzer and H. H. Liu**

Lawrence Berkeley National Laboratory

UFD EBS Telecom

October 25, 2012

Task 1. Development, Application, and Testing of Modeling Tools

- *Development of coupled THMC modeling tool for bentonite* (Jonny Rutqvist/Liang Zheng)
- *Reactive diffusive transport model including MD simulations* (Carl Steefel/Ian Bourg)

Task 2. Experimental Investigation of U Radionuclide Transport in Clay

(Jim Davis/Ruth Tinnacher)

Task 6. DECOVALEX: HE Test Modeling (Jonny Rutqvist/Jens Birkholzer)

Task 7. Long-Term Field Tracer Test (DR-A) Modeling (Carl Steefel)

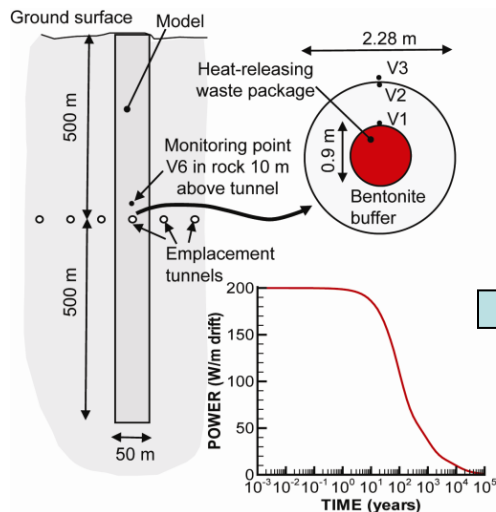
FY 13 Deliverables

- *Investigation of reactive transport and coupled THMC processes in EBS: FY13 Report (Due on 7/16/2013; Tasks 1 and 2)*
- *THM and reactive transport model development and evaluation: International activities (Due on 10/16/2013; Tasks 6 and 7)*

FY12 Work and Accomplishments

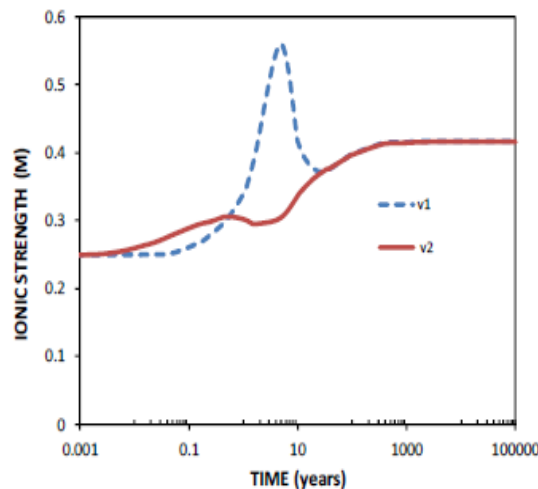
- Application of TOUGH-FLAC with BBM (Barcelona Basic Model) for modeling of coupled THM (thermal-hydrological-mechanical) processes in EBS
- THMC in TOUGHREACT-FLAC with secondary swelling is caused by changes in ionic concentration, which in turn is evaluated using a reactive transport simulation model.
- Journal paper submitted to a special issue in *Rock Mechanics and Rock Engineering*
- Implementation of double-structure model into TOUGH-FLAC (Barcelona Expansive Model)

Repository Model

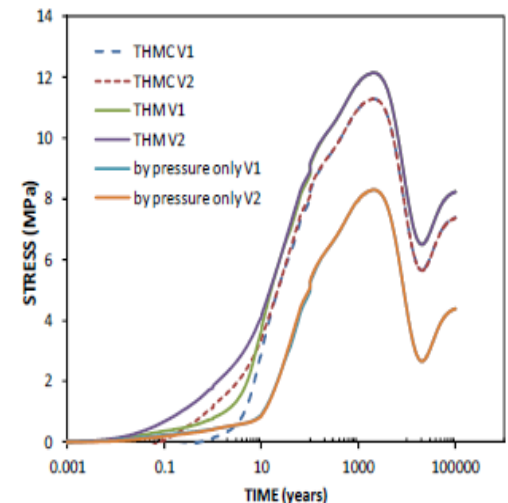


THMC

Flow and Transport

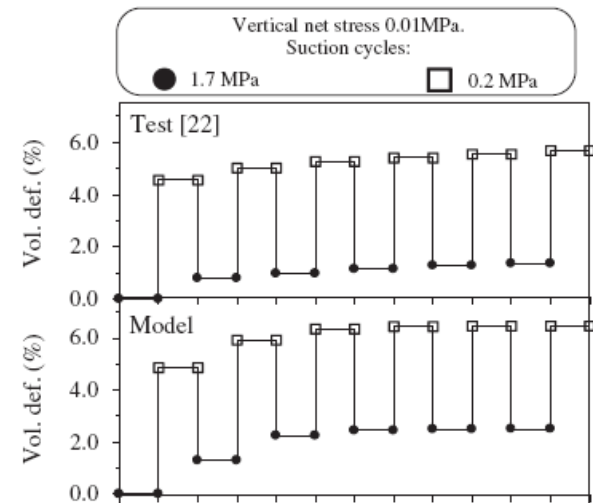
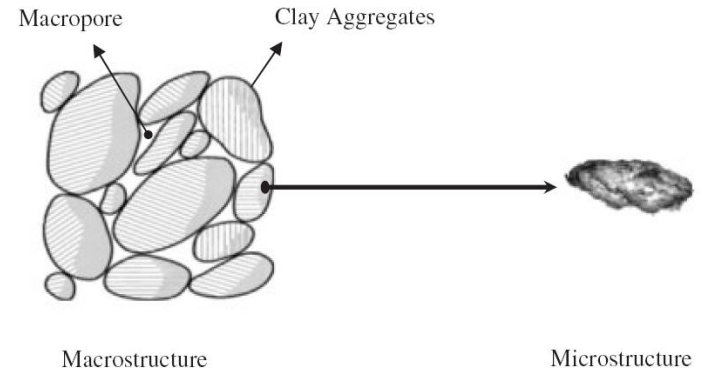
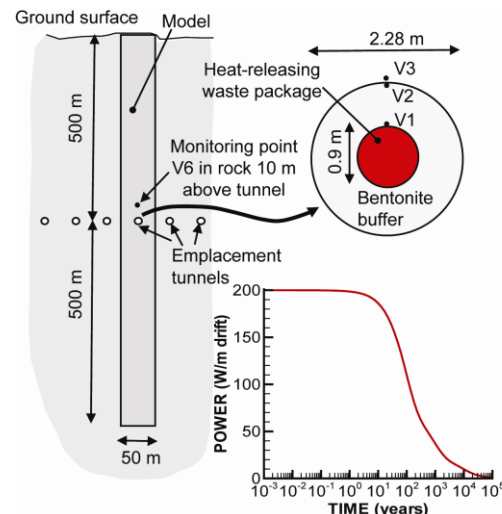


Buffer Swelling and Stress



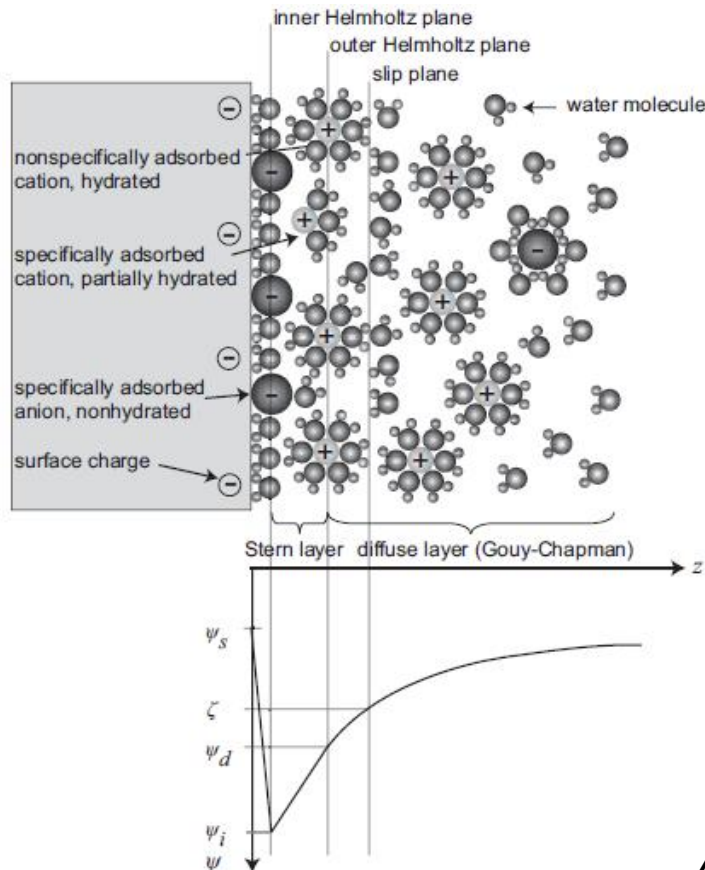
FY13 Plan

- Testing and documentation of TOUGH-FLAC dual-structure model
- Linking dual-structure model with diffuse double layer theory for the development of THMC EBS model
- Testing of THMC model against laboratory and mock-up experiments (e.g. swelling under different salinity, FEBEX mock-up)
- Application of new THMC model for generic repository cases

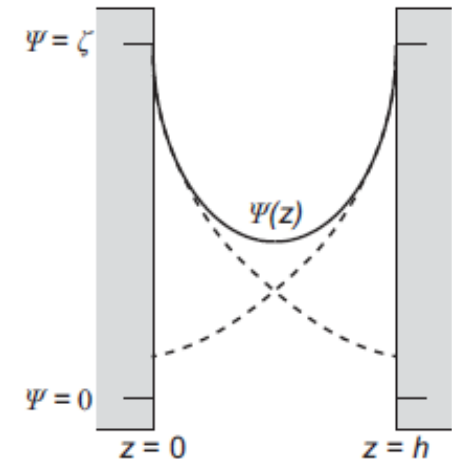


Task 1b: Reactive Diffusive Transport Model

Schematics of Electrical Double Layer



Double Layers between Charged Surfaces



Solid line: Overlapping double layers
Dashed line: No opposite wall present

After Schoch et al, 2008

Used Fuel Disposition

Mean Electrostatic (or Donnan) Potential Approach to Transport in Compacted Clay

Concentration in diffuse layer (DL)
related to concentrations in bulk water (B)
through the mean electrical potential, ϕ_m ,
of the diffuse layer

$$C_i^{DL} = C_i^B \exp\left(\frac{-z_i e \phi_m}{k_B T}\right)$$

$$\phi^{DL} \sum_i z_i C_i^{DL} = Q^{SL} = \sum_k^{Ns} z_k \Gamma_k$$

Charge Balance Equation

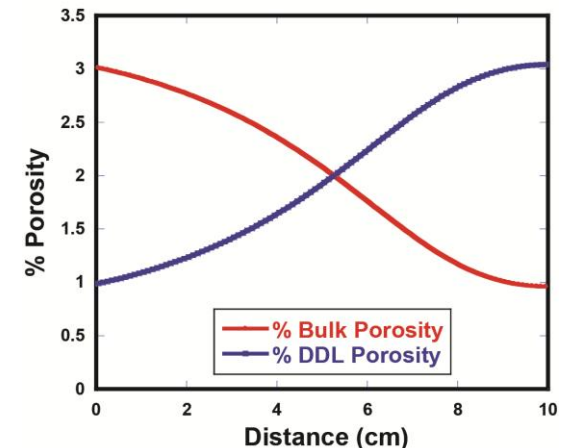
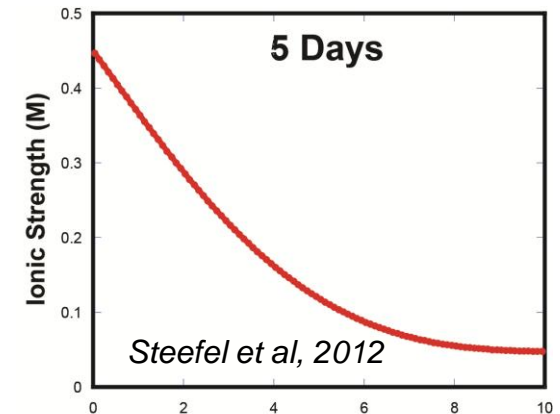
*Higher ionic strength
front diffuses through
clay, reducing EDL
porosity, increasing
bulk porosity*

Recent improvements to model

- Added ability to calculate double layer volume based on Debye length dynamically computed from ionic strength
- Developed model for inner sphere sorption of cations (no H⁺) balanced by electrical double layer

Dynamic model for electrical double layer
thickness as a function of ionic strength

$$\frac{\partial [\phi^B C_i^B + \phi^{EDL} C_i^{EDL}]}{\partial t} = \frac{\partial \left[\phi^B C_i^B + \left(A_{clay} \lambda_{DL} \beta_{DL} / \sqrt{I} \right) C_i^{EDL} \right]}{\partial t}$$

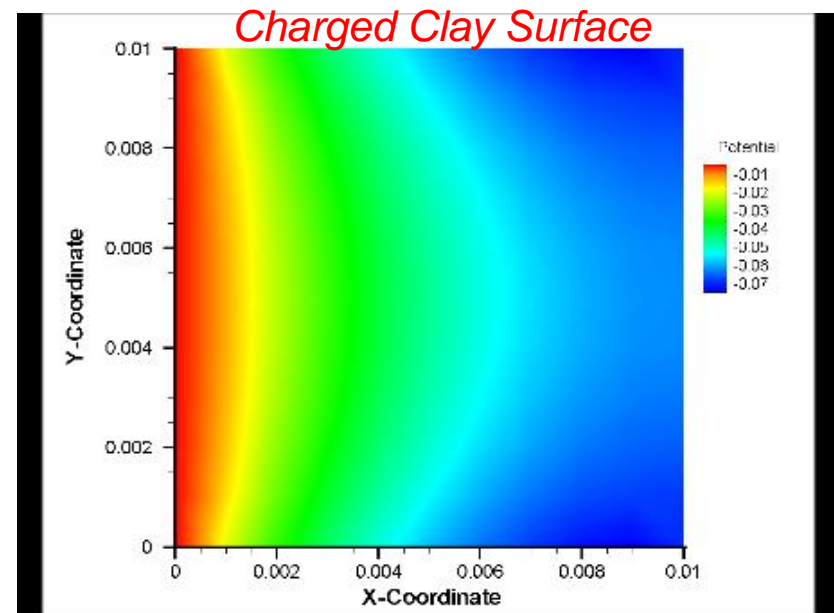


Poisson-Nernst-Planck Description of Transport through Compacted Clay

- Improved description of transport and electrical double layer is offered by solving the full Poisson-Boltzmann equation

$$\frac{\partial^2 \varphi}{\partial x^2} = \frac{-e}{\varepsilon} \sum_i z_i C_i \exp\left(\frac{-z_i e \varphi(x)}{k_B T}\right)$$

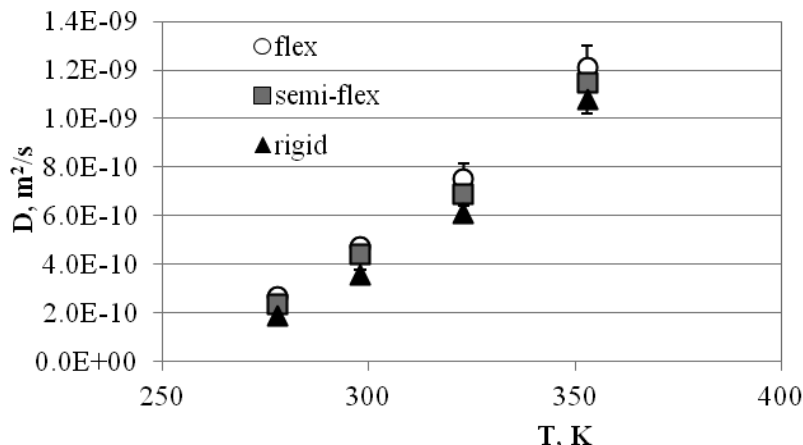
Two-dimensional cation transport between charged clay surfaces simulated with Poisson-Boltzmann Equation



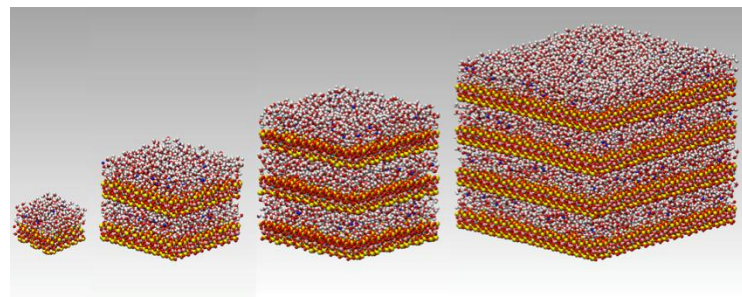
- Complete preliminary modeling of higher ionic strength diffusion test at Mont Terri DR-A site using new dynamic Debye length capability (Fall, 2012)
- Complete implementation of multicomponent Poisson-Boltzmann Equation in general purpose Reactive Transport simulator (Spring, 2013)
- Introduce calculations of the swelling pressure based on both the Poisson-Boltzmann and Mean Electrostatic (Donnan) approach (Spring 2013)
- Use Mean Electrostatic and Poisson-Boltzmann models to simulate Davis and Tinnacher experiments on uranium sorption and transport (summer 2013)

Task 1c: Ion Adsorption and Diffusion in Clay Barriers: Pore-scale studies

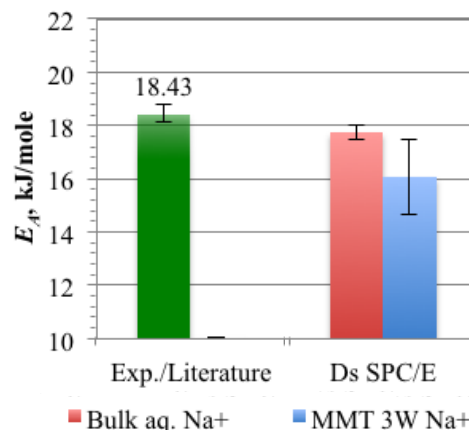
- **FY12 accomplishments:** In FY12, we carried out an extensive sensitivity analysis of the influence of simulation cell size, clay structural relaxation, and interlayer water content on molecular dynamics (MD) simulation results.
- This study led to the development of a robust methodology for simulating clay interlayer nanopores at a range of temperatures (Holmboe and Bourg, in prep.).
- Simulation results are consistent with experimental data showing that Na^+ has a lower activation energy of in the 3-layer hydrate of Na-montmorillonite than in bulk liquid water (Kozaki et al., 2005).



Simulation results show that the temperature dependence of diffusion in clay interlayers is sensitive to simulation choices such as the flexibility of the clay sheet.



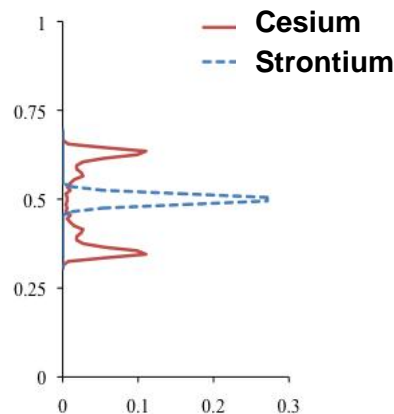
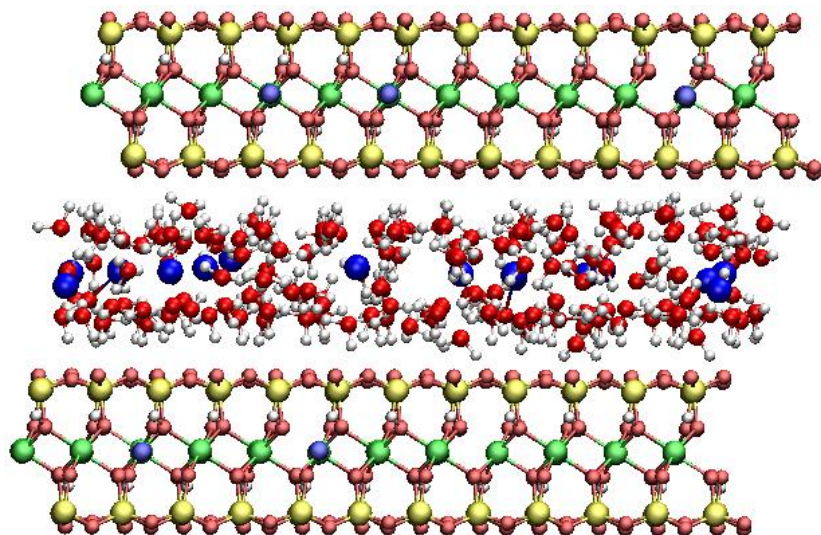
Simulation cells containing 1.3k to 136k atoms were used to test the influence of simulation cell size on predicted diffusion coefficients in Na-montmorillonite interlayer nanopores.



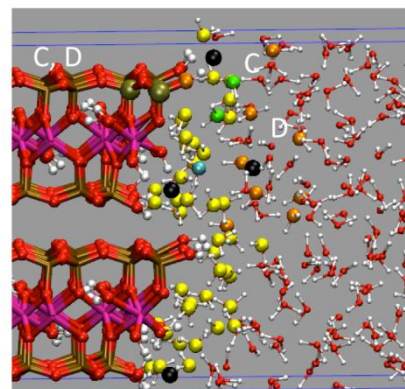
Activation energy of diffusion (E_A):
 (1) our MD simulations of Na^+ in bulk liquid water (red) are consistent with experimental data (green),
 (2) the predicted E_A value in the 3-layer hydrate of Na-montmorillonite (blue) is lower than in bulk liquid water (red).

Ion Adsorption and Diffusion in Clay Barriers: Pore-scale studies

- **FY13 research plan:** Building upon our tested methodology, we plan to carry out molecular dynamics (MD) simulations that will complement our UO_2 diffusion experiments (J. Davis) and reactive transport modeling efforts (C. Steefel).
- Our first set of simulations will determine the activation energies of diffusion of Cs^+ , Ca^{2+} , Cl^- , and UO_2^{2+} in Na-montmorillonite interlayer nanopores.
- Our second set of simulations will determine the free energy of adsorption of Cs^+ , Ca^{2+} , and UO_2^{2+} in Na-montmorillonite interlayer nanopores.



Predicted ion
density profiles



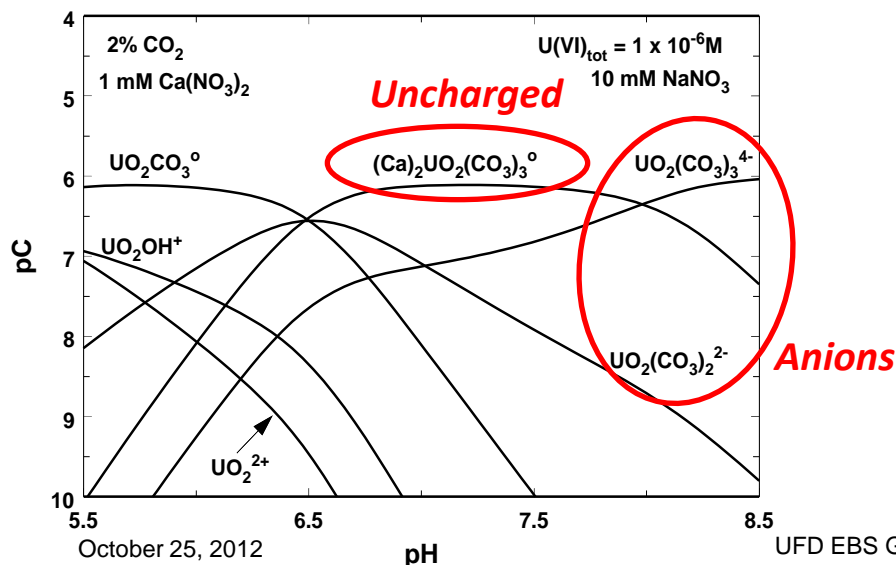
Preliminary MD simulations of Cs^+ ions (black spheres) and water molecules (different colors highlight different water layers) on clay edge surfaces (Newton, 2012, PhD thesis). Our planned work will use analogous systems with accessible, hydrated interlayer nanopores.

Simulations of Na-montmorillonite interlayers “doped” with trace amounts of UO_2^{2+} or other ions will probe the activation energy of diffusion of these species. We expect that ions that form inner-sphere surface complexes (such as Cs^+ , as shown by the density profile on the left) will have high E_A values.

Task 2: Reactive Diffusion Experiments

Research motivation and goals

- Uranium(VI) solution speciation can affect uranium diffusion rates into bentonite due to differences in charge and sorption properties of various U(VI) species.
- Important to de-couple the effects of solution speciation on sorption and diffusion processes to increase the 'predictive power' of apparent diffusion coefficients under varying chemical conditions.
- Characterize U(VI) sorption and diffusion behavior in terms of chemical conditions (pH, ionic strength, salt composition and carbonate concentration) and degree of clay compaction.



Research approach

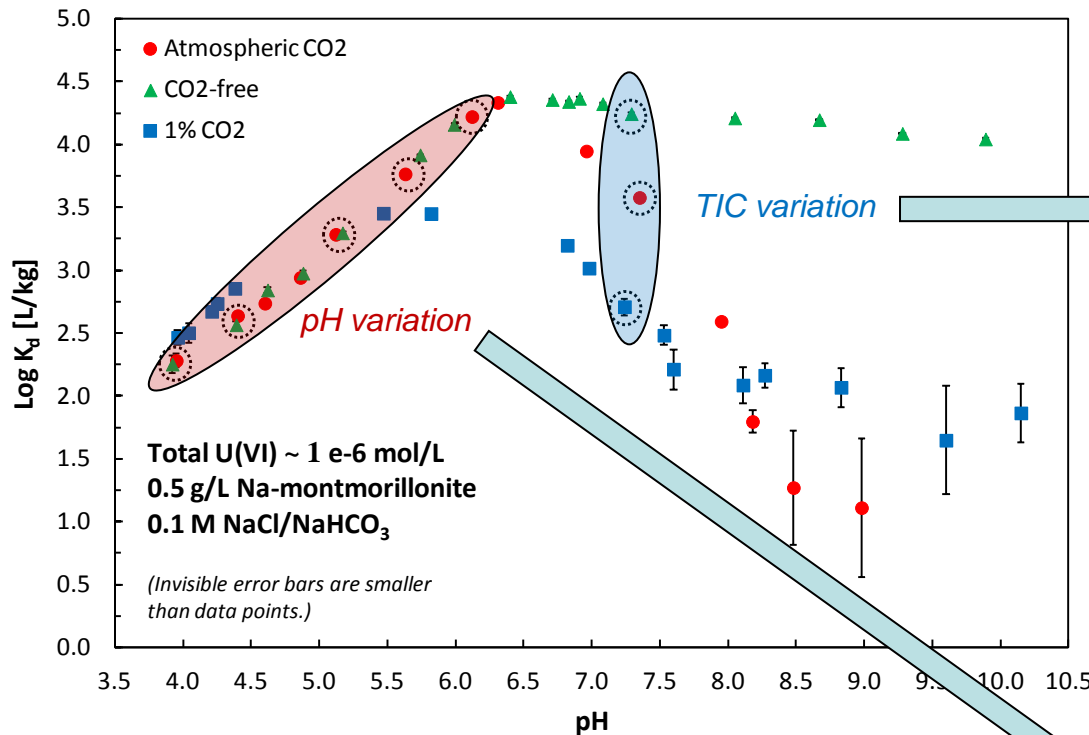
- Lab-scale experiments to evaluate U(VI) sorption and diffusion behavior.
- Collaboration with Carl Steefel and Ian Bourg (LBNL) on development of a reactive U(VI) diffusion model.

FY 2012 accomplishments

- Developed clay pretreatment method for a standardized Na-montmorillonite (Swy-2, CMS) to:
 - separate quartz and feldspar impurities,
 - minimize calcite impurities, and
 - transform clay into its Na-form.
- Performed batch sorption equilibrium experiments to evaluate U(VI) sorption to Na-montmorillonite as a function of pH and total inorg. carbonate conc.
- Used batch kinetic experiments to characterize the influence of ionic strength on U(VI) sorption kinetics onto Na-montmorillonite.
- Started development of U(VI)-montmorillonite surface complexation model.
- Designed setup for diffusion cell experiments.
- Simulated U(VI) diffusion using experimentally-determined U(VI) sorption distribution coefficients.

Example of Equilibrium U(VI) Sorption Results

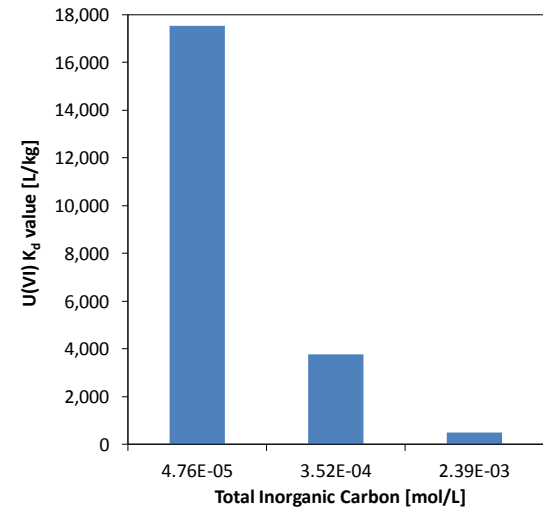
Comparison of U(VI) distribution coefficients



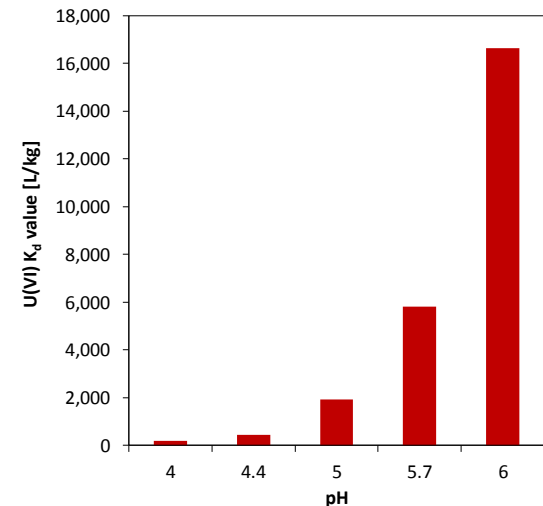
■ Goal:

- Predict U(VI) diffusion profiles as a function of pH and Total Inorganic Carbon (TIC) in a lab-scale diffusion cell.

U(VI) K_d values as a function of TIC

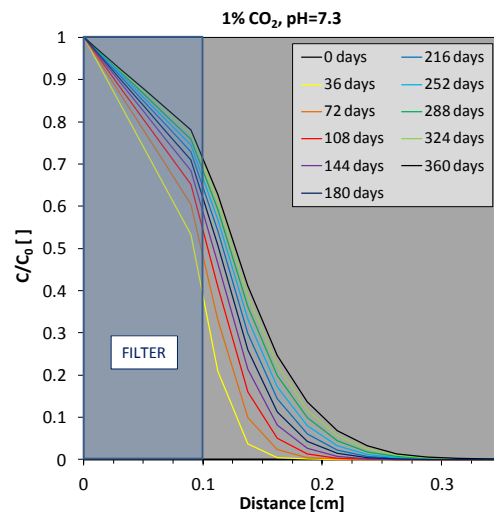
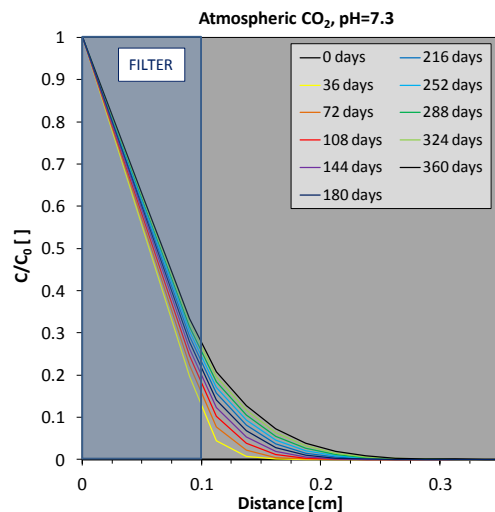
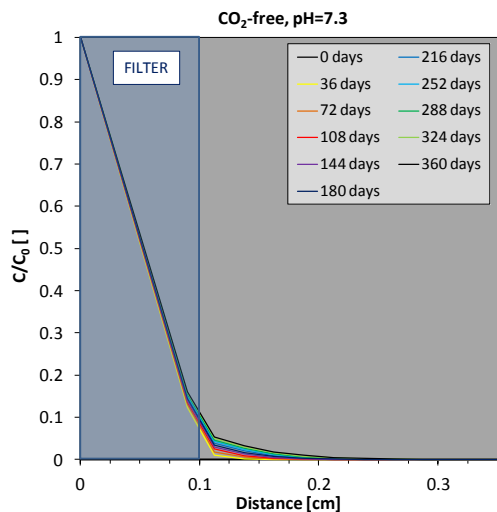


U(VI) K_d values as a function of pH

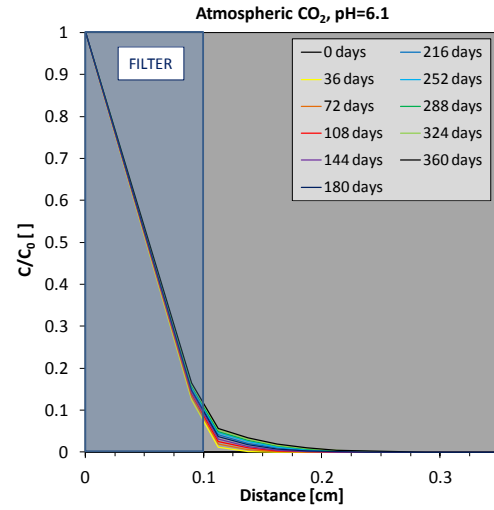
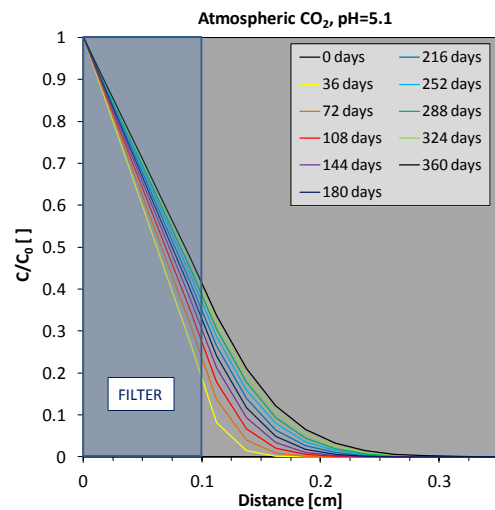
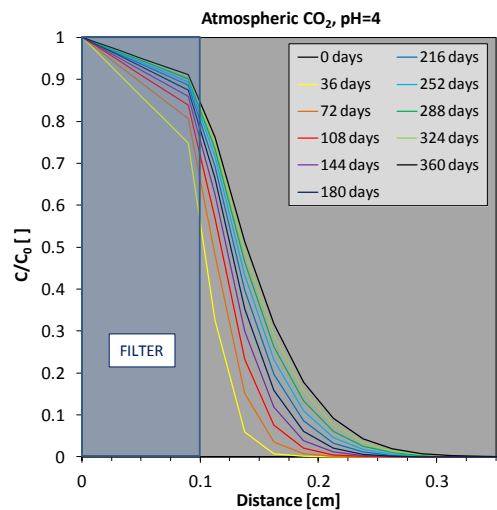


Used Fuel Disposition

Examples of Simulation Results for U(VI) Diffusion



**Increase in
Total Inorganic
Carbon
(TIC)**



**Increase in
pH**



Reactive Diffusion Experiments: FY 2013 Work Plan

■ Uranium sorption studies: Experimental and modeling

- Conduct kinetic and equilibrium U(VI) sorption experiments on montmorillonite as a function of calcium concentration.
- Conduct batch kinetic and equilibrium U(VI) sorption experiments on montmorillonite as a function of temperature.
- Complete/refine the surface complexation model for U(VI) sorption on montmorillonite by incorporating all experimental data.



■ Uranium diffusion studies: Experimental and modeling

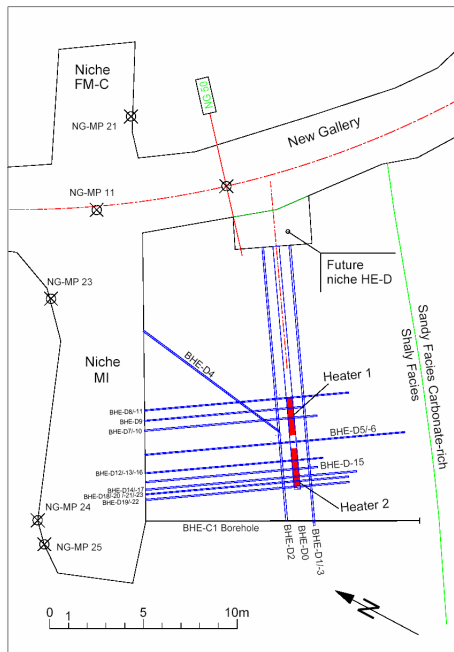
- Complete fabrication of diffusion cells for the study of U(VI) diffusion into montmorillonite and bentonite.
- Conduct study of Br^- and Ca^{2+} diffusion into montmorillonite at low compaction and at pH 7 in 0.1M NaCl solutions equilibrated with air.
- Conduct studies of U(VI) diffusion into montmorillonite at low compaction and
 - at low pH (5.0),
 - circumneutral pH (7.0) and
 - high pH (8.5)in 0.1M NaCl solutions equilibrated with air.
- Conduct study of U(VI) diffusion into montmorillonite at low compaction at pH 7 in 0.1M NaCl/1 mM CaCl_2 solution equilibrated with air.
- Conduct study of U(VI) diffusion into montmorillonite at intermediate and high compaction at pH 7 in 0.1M NaCl/1 mM CaCl_2 solution equilibrated with air.
- Engage in modeling collaborations with Carl Steefel and Ian Bourg (LBNL) on development of a reactive U(VI) diffusion model.

Task 6: Mont Terri HE Test Modeling

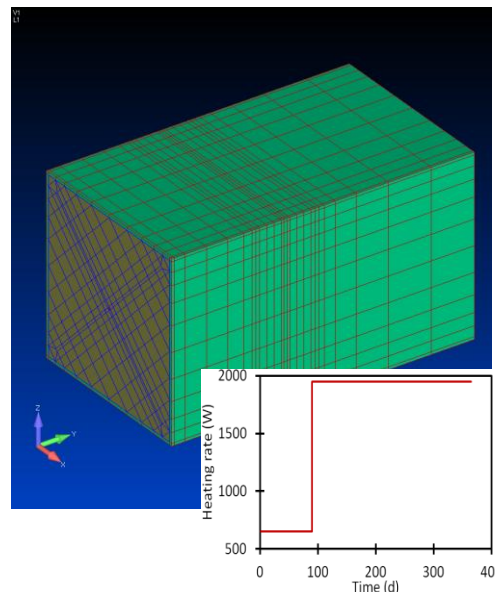
FY12 Work and Accomplishments

- 1st DECOVALEX 2015 Workshop, Berkeley, April 17-19, 2012
- 1st task is modeling previous Mont Terri rock mass HE-D heater test for calibration of THM rock properties
- Opalinus Clay thermal properties (anisotropic) back-calculated and thermal pressurization validated

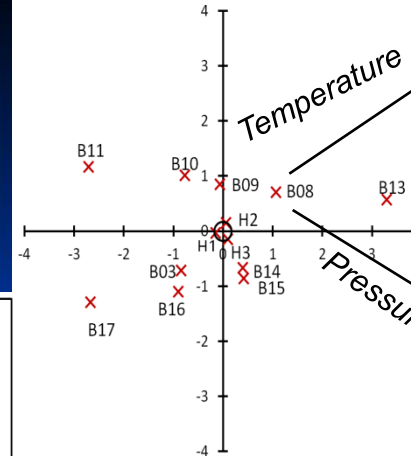
Plane view of HE-D test at Mont Terri



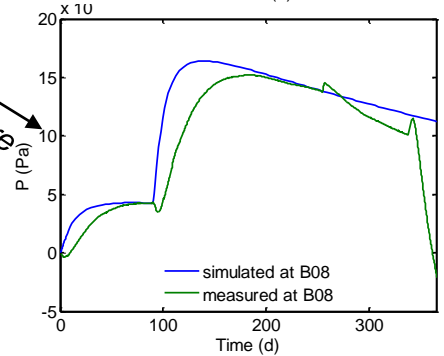
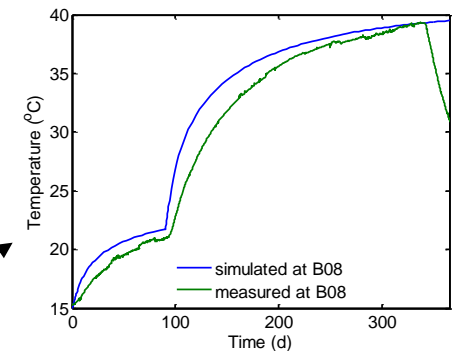
3D TOUGH-FLAC model



Vertical cross-section showing sensor locations



Simulated vs observed



FY13 Plan

- 2nd DECOVALEX 2015 Workshop to be held in Leipzig Germany, November 6-9, 2012 (present results on HE-D test)
- Buffer material study of THM experimental data provided by DECOVALEX to determine and calibrated buffer properties (until October 2013)
- Develop 3D TOUGH-FLAC THM model of HE test

Laboratory Experiment for buffer material study (example)

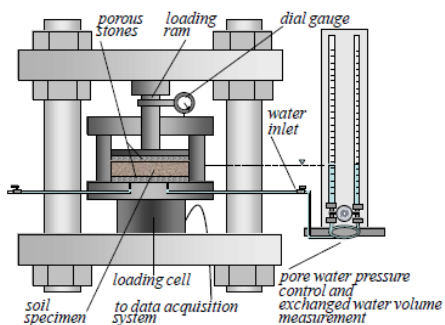
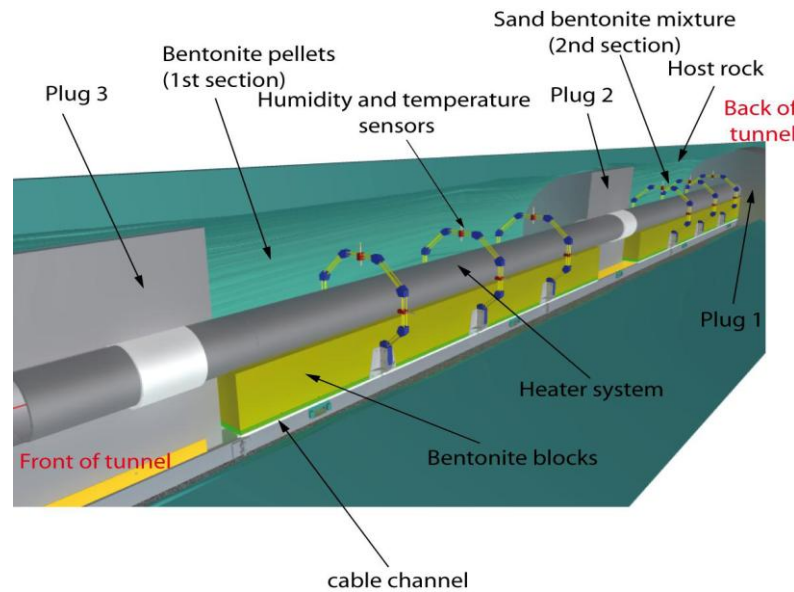


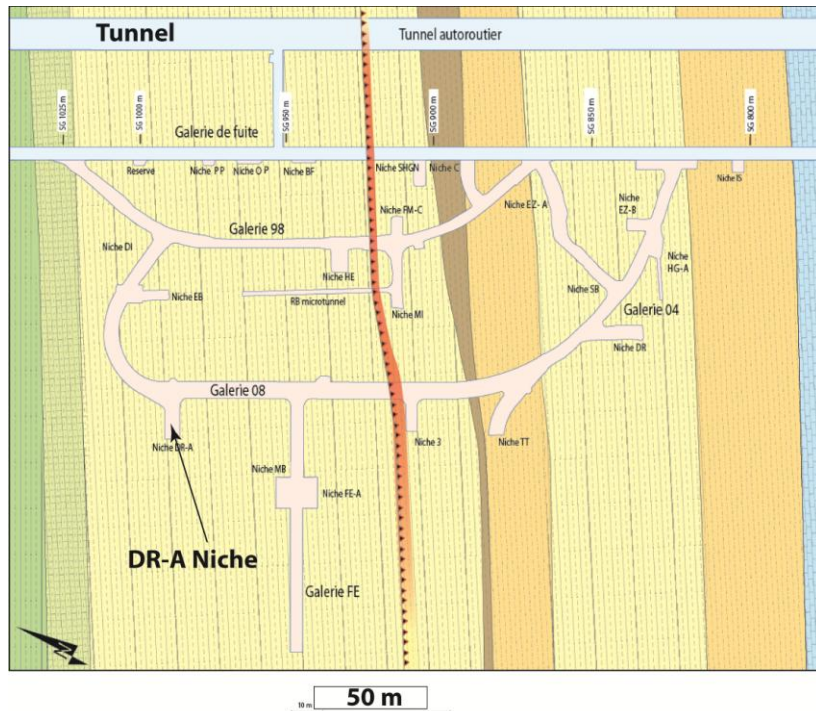
Figure 3.18 – Confined swelling test device: schematic cross section and picture of the cell used. The piston of the cell is designed in order to avoid bentonite leaking and to permit a good measurement of the swelling pressure.

(Rizzi et al 2012)

HE test layout

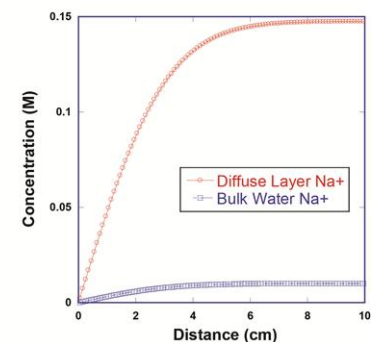
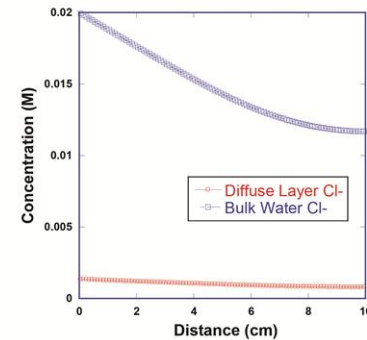


Task 7. Modeling of DR-A Diffusion Test at Mont Terri

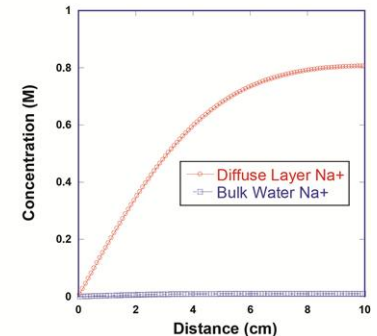
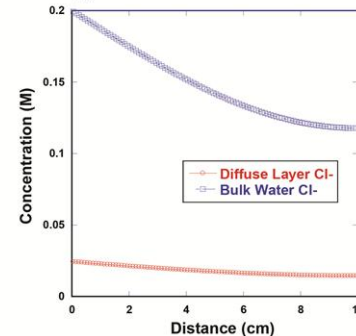


Mont Terri map with location of DR-A Test

Ionic Strength = 0.04 M



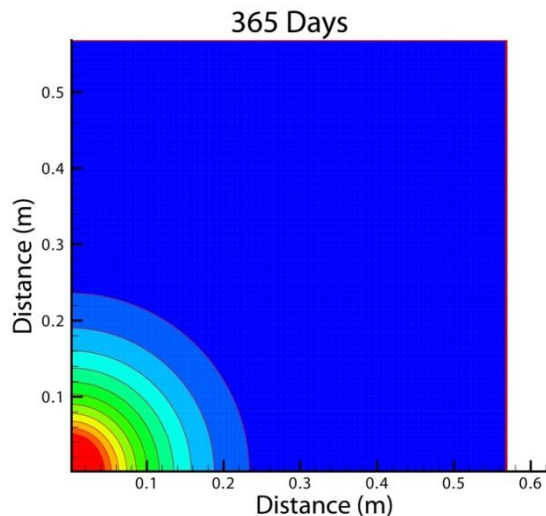
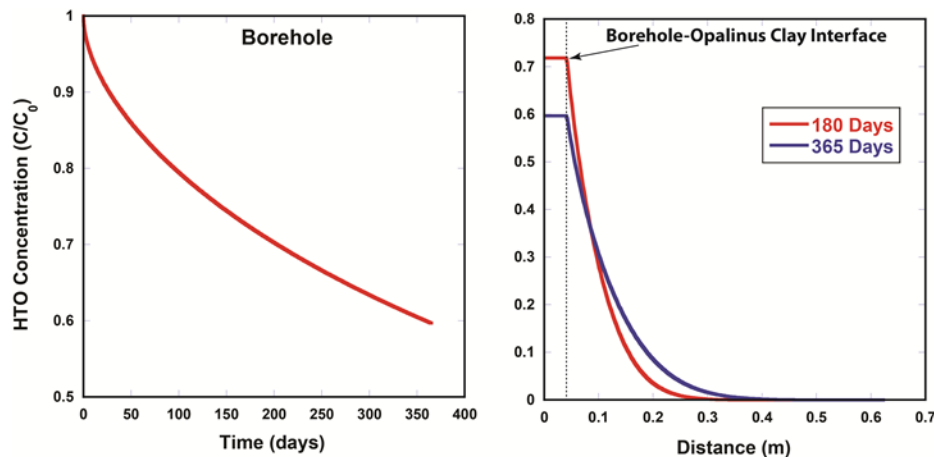
Ionic Strength = 0.4 M



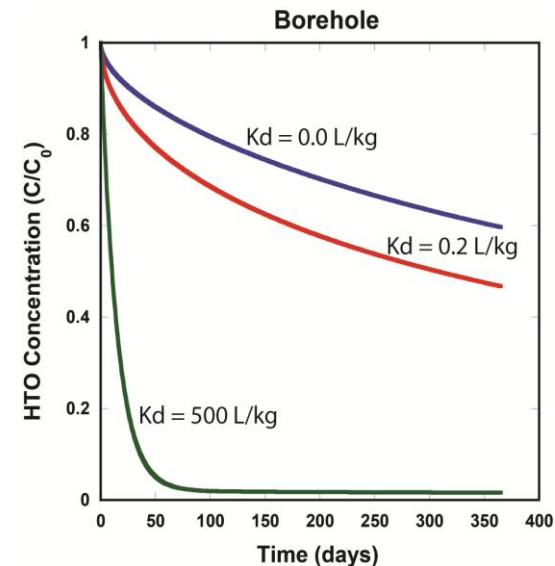
Next Step:

Simulate higher ionic strength migration test at Mont Terri using fixed and dynamic Debye length capability (as a function of ionic strength)

Test Problem 1: Non-Reactive Tracer



Test Problem 2: Effect of K_d on Cs^+ Transport



***Test problems are part of the suite
agreed upon by International
Consortium modeling DR-A test***

- **Complete preliminary modeling of higher ionic strength diffusion test at Mont Terri DR-A site using new dynamic Debye length capability (Fall, 2012)**
- **Compare results with other groups, including Canada, France, Switzerland, Spain (Spring and Fall, 2013)**
- **Complete modeling of full DR-A injection, which is underway now (Summer, 2013)**
- **Generalize results to migration in clay-rich materials (including compacted bentonite).**